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Research and Development Report

DEVELOPMENT OF ASTM D2274 REFERENCE FUELS BASED ON 1,2,5 TRIMETHYLPYRROLE IN n-DODECANE

INTERIM REPORT
EFFECT OF PREPARATION PROCEDURES AND TRIMETHYLPYRROLE AGING

by
Dr. M.D. Klinkhammer

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Interim Report: Effect of Preparation Procedures and Trimethylpyrrole Aging

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Solutions of 1,2,5-trimethylpyrrole (TMP) in n-dodecane were evaluated for use as reference fuels to produce known amounts of sediment. Tests were run in accordance with ASTM D2274, "Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)." Each of four test operators determined the amount of sediment formed as a function of TMP concentration (0 to 150 milligrams per 100 milliliters) and of D2274 stress time (4 to 96 hours).

Results from the four operators were not in good agreement, probably due to the following factors. Some operators used TMP from freshly opened bottles; others used TMP from bottles that had been opened and refrigerated for a considerable length of time. Also, there were differences in the technques used to prepare the TMP solutions, in the filter media used, and in operator precision. Gas chromatographic analysis of selected prestressed fuel samples indicated that the stated concentrations were not always accurate.

Further tests to obtain a better definition of the usefulness of solutions of TMP in n-dodecane as reference fuels should concentrate on (1) stricter control of procedural and material factors (e.g., fuel preparation and TMP age) and (2) the range of D2274 insolubles of most interest to MIL-F-16884 users, namely 0 to 3 milligrams per 100 milliliters (i.e., initial TMP concentrations of <50 milligrams per 100 milliliters).

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ABBREVIATIONS

ASTM	American Society for Testing Materials
Avg	Average
^{o}C	Degrees Celsius
FID	Flame ionization detector
g	Grams
GC	Gas chromatograph
μm	Micrometer
mg	Milligrams
mL	Milliliters
NPD	Nitrogen/phosphorous detector
TMP	1,2,5-trimethylpyrrole

ABSTRACT

Solutions of 1,2,5-trimethylpyrrole (TMP) in n-dodecane were evaluated for use as reference fuels to produce known amounts of sediment. Tests were run in accordance with ASTM D2274, "Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)." Each of four test operators determined the amount of sediment formed as a function of TMP concentration (0 to 150 milligrams per 100 milliliters) and of D2274 stress time (4 to 96 hours).

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This work was block-funded to this Center by the Office of Naval Research (Dr. Alan Roberts, Code 12E) under Program Element 63724N, Task Area RO838, and Center Work Unit 2759-803. Mr. W.H. Stoffel of the Shipboard Energy Research and Development Office at this Center (Code 2759) was the block program manager, Mr. R. Strucko (Code 2759) was the project engineer, and Dr. E.W. White (Code 2832) was the technical manager.

INTRODUCTION

The stability of Naval Distillate Fuel MIL-F-16884 is evaluated using procedures described in ASTM D2274, "Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)." One of our goals was to improve the poor reproducibility of this specification test, a condition that has been attributed to a number of factors. One is that unless samples of the same fuel are shipped and stored under the same conditions and for the same length of time, a variance will occur in the samples tested and the results obtained. Differences in the apparatus used, test procedures, and analyst experience also may cause the test results to vary. It is useful to have reference fuels of known fixed composition and stability to determine whether these factors are a source of variance. Such fuels could be used as blind samples for quality control checks, to train operators, and to check new or existing D2274 apparatus.

We felt that reference fuels based on refinery products would be difficult to reproduce; hence, we based our reference fuels on a few pure chemical compounds. While several sediment-forming compounds were considered originally, 1,2,5-trimethylpyrrole (TMP) was found to be the most suitable based on its availability, stability, and solubility. Originally, we blended TMP in a base fuel of n-dodecane, t-amylbenzene, and 1-dodecene such that the proportion of saturates, aromatics, and olefins was comparable to that found in typical MIL-F-16884 fuels[1]. The t-amylbenzene became scarce and too costly so cumene was evaluated briefly as a possible aromatic substitute. Subsequently, we have been using only TMP in n-dodecane to simplify procurement and blending of the reference fuel.

This report describes the progress of tests being conducted to evaluate the use of TMP as a reference fuel in n-dodecane and to develop calibration curves of insolubles versus TMP concentration and stress time.

EXPERIMENTAL

EQUIPMENT AND MATERIALS

Heating Bath

All operators conducting the ASTM D2274 tests used the same 12-cell heating bath* described previously.[2] The bath has a continuous heater control (low, medium, or high setting) and a thermostatically controlled heater (vernier setting). Total heating power available is 3750 watts, and the bath contains about 72 liters of low viscosity silicone oil. Several tests were run with thermocouple probes in a tube and in the bath fluid because the temperature recovery time for a bath upon insertion of D2274 test tubes is a factor in test precision.

Gas Chromatograph

In some of the reference fuel samples, the concentration of 1,2,5-trimethylpyrrole was measured using a Hewlett Packard Model 5880 gas chromatograph (GC) with autoinjector, an HP-1 methyl silicone capillary column (12-m x 0.2-mm x 0.33-μm film thickness),** and split-column effluent to a flame ionization detector (FID) and nitrogen/phosphorous detector (NPD).

Chemicals

Table 1 lists the chemicals used, their typical purities, their source, and container size.

TMP degrades more rapidly in a bottle that has been opened and exposed to air. Therefore, smaller bottles of TMP were preferable to ensure that the TMP used in each test was fresher and of more uniform quality.

The higher purity adherent gum solvents (B&J brand) had less residue after evaporation and gave lower adherent insoluble blanks.

*Manufactured by Koehler Instrument Co., Inc., 1595 Sycamore Ave., Bohemia, Long Island, NY 11716.

**Hewlett-Packard Co., Analytical Supplies Operation, P.O. Box 1000, Avondale, PA 19311-9981.

Table 1. Description of chemicals used.

Chemical	Typical Purity	Source	Container Size
TMP	97%*	Aldrich Chemical Co.**	5 or 25 g bottle
n-dodecane	Technical grade	Humphrey Chemical Co.***	5-gallon can
Isooctane	ASTM knock test reference	Phillips 66 Co.#	54-gallon drum
Acetone	>99.9%	Burdick & Jackson##	1-gallon drum
	AR grade	Mallinkrodt♦	54-gallon drum
Methanol	>99.9%	Burdick & Jackson	1-gallon bottle
	Certified ACS	Fisher Scientific♦♦	5-gallon can
Toluene	>99.8%	Burdick & Jackson	1-gallon bottle
	Certified ACS	Mallinkrodt	1-gallon bottle

*Aldrich lists the typical purity of their TMP as 97% in their 1986-87 catalog but 99% in their 1990-1991 catalog.
**1001 West St. Paul Ave., Milwaukee, WI 53233.
***Devine St., North Haven, CT 06473.
#P.O. Box 968, Borger, TX 9008-0968.
##Division of Baxter Healthcare Corp., 1953 S. Harvey St., Muskegon, MI 49442.
♦50 Fadem Rd., Springfield, NJ 07081.
♦♦675 McDonnell Blvd., St. Louis, MO 63134.

PROCEDURES

Fuel Preparation

Four operators conducted the D2274 tests at this Center. Operators 1 and 2 were Center employees and Operators 3 and 4 were contracted to perform the tests using the same apparatus. Each operator prepared his or her own fuels for testing. Operators chose somewhat different techniques because a detailed procedure for preparing reference fuels for this work had not been specified.

For each run of 12 tubes, Operators 1 and 2 weighed TMP from previously unopened, refrigerated 5-gram bottles into a tared volumetric flask containing some n-dodecane. Next, the volumetric flask was filled to the mark with n-dodecane to produce a known concentrate. The volumetric flask was inverted several times to ensure thorough mixing. Then aliquots were pipetted from the concentrate and diluted to the desired concentrations with n-dodecane.

Operators 3 and 4 performed the D2274 tests using the Center's D2274 apparatus but with chemicals which they had obtained. In preparing the reference fuels, Operators 3 and 4 calculated the TMP volume required (based on TMP density) to make the concentrations desired for each tube. They used a micropipette or syringe to take each volume of TMP directly from a 25-gram bottle of TMP and added it to the required volume of n-dodecane to make each of the desired concentrations. They kept the unused portion of the 25-gram bottle refrigerated for subsequent runs.

ASTM D2274

Insolubles formed were determined using ASTM D2274-88 with the following exceptions. Operator 1 used glass fiber filters, listed as 1.6-μm porosity (Gelman type A/E*), and a drying temperature of 110°C vice the 0.8-μm porosity cellulose ester filters and 80°C drying temperature specified by the method. Operator 2 used the same filters and drying temperature as Operator 1 for the concentration series of tests but used the D2274-88 specified filters for the time series (tests other than 16-hr duration). Operator 2 conducted D2274 tests in triplicate; the other operators obtained duplicates.

Gas Chromatography Analysis

TMP concentration was determined as a function of D2274 test time by taking approximately 2-mL fuel samples at the start and end of selected D2274 tests, and refrigerating all samples. When all of the samples from a time series of runs had been collected, GC was

*From Fisher Scientific, 50 Fadem Road, Springfield, NJ 07081.

used to analyze for TMP. Suitable analytical techniques were developed by calibrating prepared concentrations against (1) a flame ionization detector (FID) peak height ratio of the TMP peak to a n-dodecane contaminant peak, or (2) the peak height of TMP using a nitrogen-phosphorous detector (NPD). Analyses of samples by the FID method were quite repeatable with an average standard deviation of about 1% of the concentration. The NPD method was able to detect lower concentrations of TMP. An average of the concentration values obtained by each detector was used to obtain the results in this report.

Test Plan

Our test plan called for four operators to prepare solutions of TMP in n-dodecane and determine the amount of insolubles formed by ASTM D2274 as a function of TMP concentration and test duration. Curves then would be generated to inform the D2274 user as to the amount of insolubles that should be obtained for a particular TMP concentration and test duration.

Further, the plan was to determine the variability of operator techniques and the sensitivity of TMP's sediment forming rate to such factors as air exposure, refrigerated storage, and elapsed time from purchase to use. Four operators conducted the tests to help point out any other factors that may need to be controlled to ensure reproducible results using a reference fuel. Any variability due to operator or material differences may be determined in this manner. ASTM round-robin tests could be used to determine any variability due to apparatus or laboratory differences.

Finally, the plan was to use GC analysis to check the purity of the TMP batches, the accuracy of TMP concentrations in prepared reference fuels, and the loss of TMP with time in D2274.

RESULTS AND DISCUSSION

Complete data obtained by the four operators are contained in Appendix A. Differences such as the age of the TMP, the type of filter used, and the experience level of the operators are likely contributing factors to the variance in results among operators.

A variance was calculated for replicate runs by each operator on each test fuel. As an indication of repeatability by the same operator, the average of these variances for each operator along with the number of tests performed is shown in Table 2. All operator variances differed significantly from each other except the average variances for Operators 3 and 4 (when tested at the 95% confidence level using the F-distribution test for equality of two population variances). The large variance of Operator 2 resulted primarily from 4 of the 26 runs. The average variance of Operator 2 would be reduced to 0.73 if those four runs were not included (still a significant figure).

Table 2. Testing by operators.

Operator	Number of Replicate Runs	Average of Variances
1	14	0.04
2*	26	5.87
3	24	0.51
4	23	0.22

*Operator 2 usually conducted tests in triplicate; other operators conducted tests in duplicate.

Temperature monitoring of the test bath and test fuel showed that the fuel reached test temperature within 30 minutes after placing the 12 tubes of room-temperature fuel into the 95°C bath. Figure 1 shows typical plots of bath and fuel temperatures as a function of time.

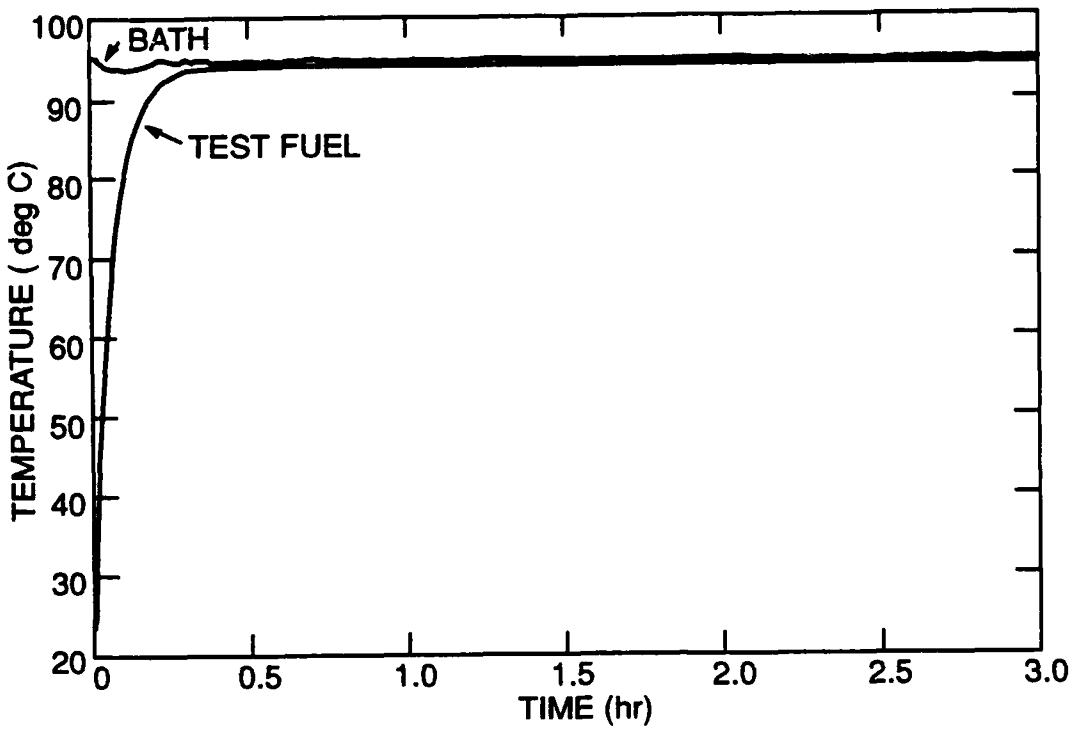

Fig. 1. Temperature of test fuel and bath versus test duration.

INSOLUBLES VERSUS TMP CONCENTRATION

Total insolubles produced as a function of TMP concentration in standard 16-hr D2274 tests are shown in Table 3 and Figure 2 for each operator. The average total insolubles value for each concentration and operator and the replicates are listed in Table 3. The expected repeatability and reproducibility (as given in D2274 test precision for the total insoluble levels obtained) are included in Table 3 also. In the case of repeatability, the difference between two test results obtained by the same operator with the same apparatus, constant operating conditions, and identical test material, would exceed the values only in 1 out of 20 tests assuming correct operation of the test method. For reproducibility, the difference between two single and independent results obtained by different operators working in different laboratories on identical test material also would only exceed the calculated values in 1 case in 20, assuming correct operation of the test.

Table 3. Total insolubles versus initial TMP concentration.

Initial TMP Concentration (mg/100 mL)	Avg Total Insolubles (mg/100 mL)	Operator	ASTM D2274		Replicates Insolubles (mg/100 mL)
			Repeat-ability	Reproduc-ibility	
0.00	0.31	1	0.40	0.79	0.33, 0.28
0.00	0.46	2	0.44	0.87	0.60, 0.39, 0.40
0.00	0.04	3	0.24	0.47	0.05, 0.03
0.00	0.12	4	0.32	0.62	0.25, -0.02
15.59	0.44	2	0.44	0.86	0.52, 0.40, 0.39
17.43	0.40	2	0.43	0.84	0.35, 0.42, 0.42
20.00	0.75	4	0.50	0.99	0.81, 0.68
24.00	0.83	3	0.52	1.01	0.90, 0.75
24.00	0.87	4	0.52	1.02	1.01, 0.73
24.14	0.69	1	0.49	0.97	0.71, 0.66
31.17	0.51	2	0.46	0.90	0.51, 0.43, 0.59
34.86	0.89	2	0.52	1.03	1.28, 0.93, 0.47
40.00	2.30	4	0.67	1.31	2.26, 2.33
48.29	2.80	1	0.70	1.37	2.60, 3.00
49.00	3.77	3	0.75	1.48	3.66, 3.88
49.00	3.30	4	0.73	1.43	3.11, 3.49
60.00	5.93	4	0.84	1.65	5.13, 5.51, 6.34, 6,72
62.34	3.21	2	0.72	1.42	4.20, 2.41, 3.03
69.71	4.75	2	0.80	1.56	4.89, 4.98, 4.29
72.43	6.31	1	0.86	1.68	6.52, 6.10
75.00	9.53	3	0.95	1.86	10.07, 8.98
75.00	8.40	4	0.92	1.80	8.21, 8.59
96.57	10.13	1	0.96	1.89	10.13, 10.13
98.00	16.33	3	1.09	2.13	16.48, 16.18
98.00	13.18	4	1.03	2.02	13.56, 12.80
104.57	11.31	2	0.99	1.94	10.53, 11.39, 12.01
120.71	17.44	1	1.10	2.17	17.63, 17.25
150.00	31.97	3	1.28	2.52	31.90, 32.03

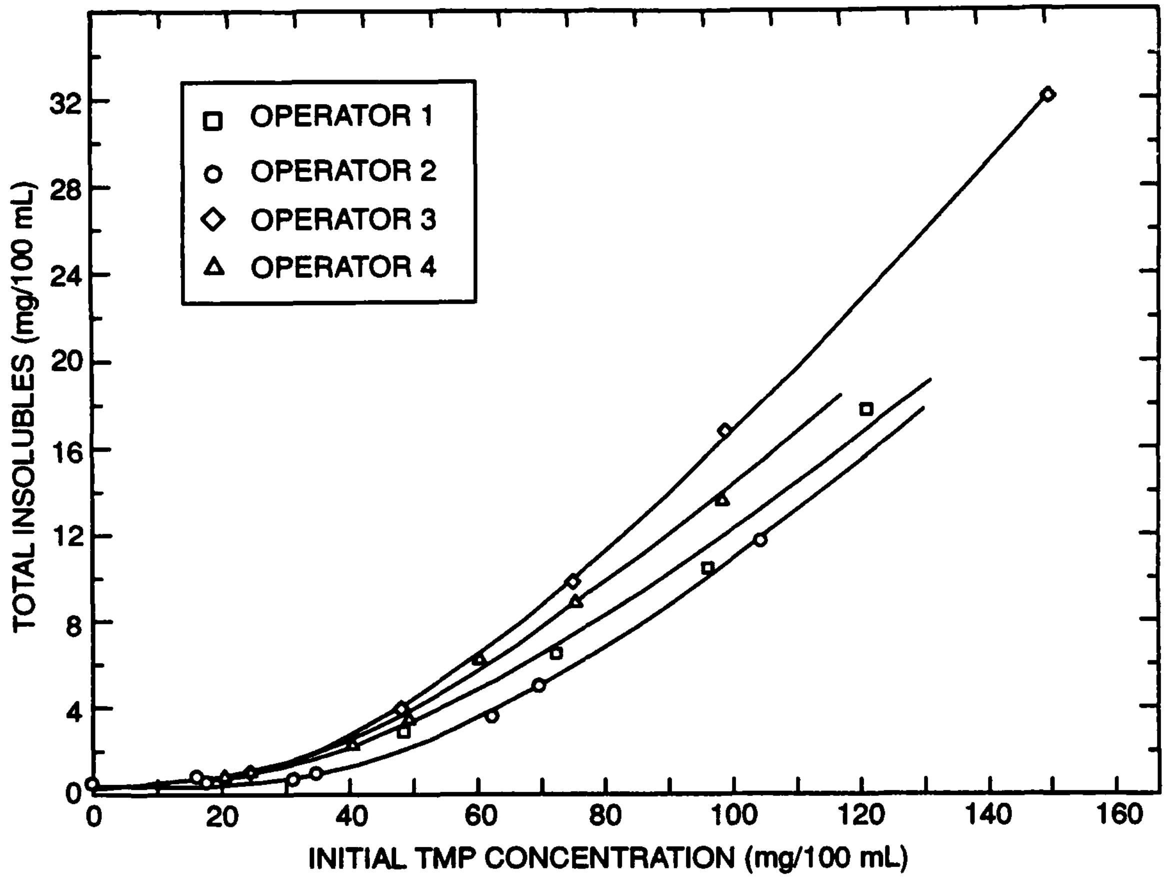

Fig. 2. D2274 total insolubles versus initial TMP concentration.

In the standard 16-hr D2274 tests of Table 3, Operators 1 and 3 had no duplicate runs that exceeded D2274 repeatability limits. Operator 4 had one run that exceeded repeatability, the 60 mg/100 mL initial TMP concentration run. Operator 2 had three triplicate runs that exceeded repeatability limits -- 34.86, 62.34, and 104.57 mg/100 mL initial TMP concentration.

The following results are obtained when D2274 repeatability limits are applied to all tests, including those with stress times different than the standard 16 hr given in Appendix A. All 16 duplicate runs conducted by Operator 1 were within D2274 repeatability. Operator 2 had 17 of 26 replicate runs where values exceeded D2274 repeatability; Operator 3 had 5 of 24 runs, and Operator 4 had 6 of 23 replicate runs. Improved repeatability would make it easier to discern factors contributing to poorer reproducibility among operators.

We do not have a true measure of reproducibility in our work because all operators used the same stability test apparatus in the same laboratory. Indeed, we expected to obtain reproducibility at least equal to that given in the method because all operators were using the same apparatus. However, Table 3 shows that some of the operators' results at the same (or approximately equal) concentrations exceed D2274 reproducibility values, particularly at higher TMP concentrations.

Operators 3 and 4 used TMP from a 25-gram bottle. Consequently, their runs exposed TMP to air for differing times before it was used in the D2274 tests. Figure 2 shows that Operators 3 and 4 obtained larger amounts of insolubles than Operators 1 and 2 who used fresh TMP from 5-gram bottles opened just prior to D2274 tests. The slightly higher porosity of the glass fiber filters used by Operators 1 and 2 could also be a factor in the lower insolubles they obtained. The reproducibility of these runs is not adequate to obtain a satisfactory curve of TMP concentration versus D2274 insolubles.

To study the effect of TMP aging on D2274 insolubles, Operator 4 conducted standard 16-hr D2274 tests on two sets of duplicate samples containing 20, 40, and 60 mg TMP/100 mL; all samples were run in duplicate. One set was prepared using TMP that had been refrigerated; the aged set was prepared from TMP taken from the same bottle but maintained room temperature for 1 week. The aged TMP produces more D2274 insolubles; see Table 4 and Figure 3. It is clear that TMP exposure to air and heat should be avoided prior to D2274 tests. We conclude that reference fuels should be prepared using TMP from freshly opened bottles only.

Table 4. Effect of TMP aging on insolubles.

Initial TMP Concentration (mg/100 mL)	Total Insolubles (mg/100 mL)	
	Fresh	Aged
20.0	0.75	1.85
40.0	2.30	6.29
60.0	5.93	11.52

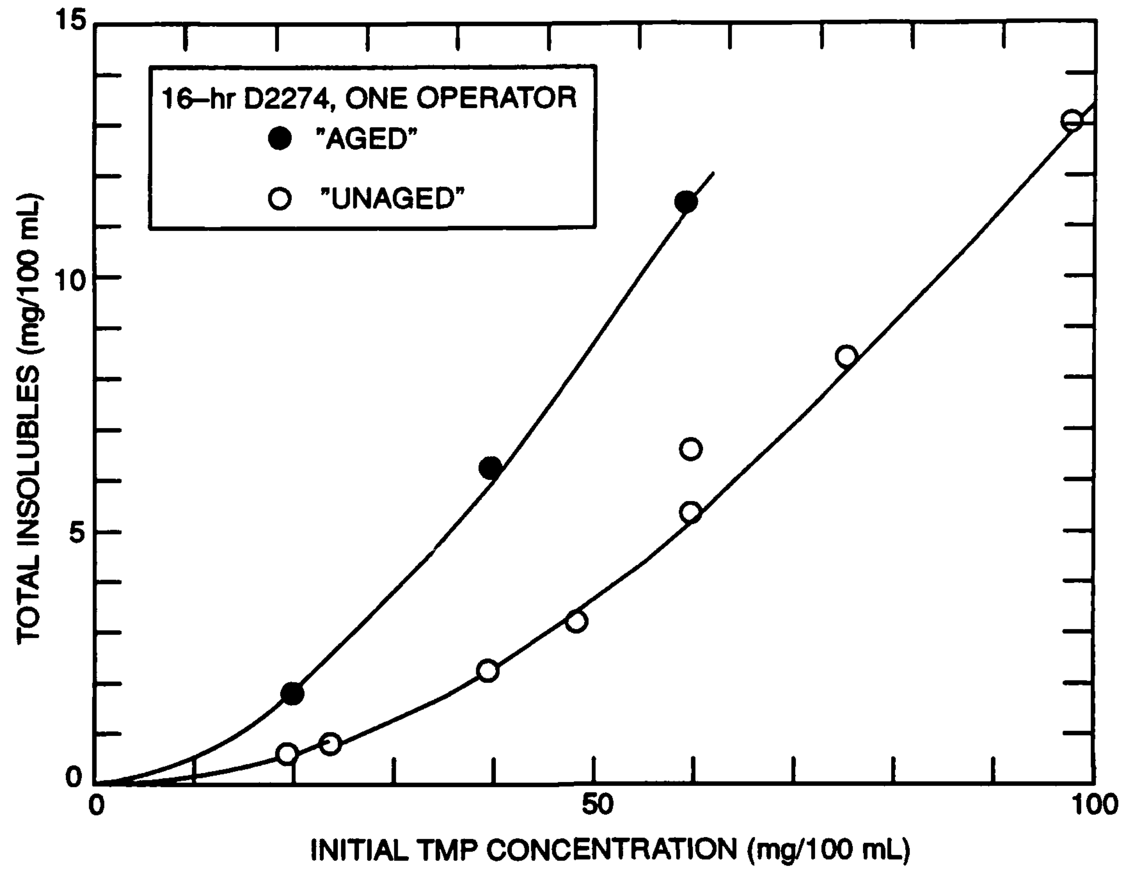

Fig. 3. Effect of TMP freshness on D2274 insolubles.

INSOLUBLES VERSUS TEST DURATION

The formation of D2274 insolubles as a function of test time is shown for three different initial TMP concentrations in Figures 4 through 6. The data for these curves are given in Tables 5 through 7. Again, in most instances, Operator 3 obtained higher amounts of insolubles than the other operators, probably due to TMP aging.

Only small amounts of insolubles are formed at test times of 8 hr or less. We noted from GC analysis that the concentration of TMP appears to decrease little in the first 4 hr of the D2274 test. This apparent induction time may be less for TMP that has been exposed to air for a significant time before conducting the tests.

Table 5. Total insolubles versus D2274 test duration; initial TMP concentration of 24 mg/100 mL.

Test Duration (hr)	Total Insolubles (mg/100 mL)			
	Operator			
	1	2	3	4
4	-	0.72	0.12	0.59
8	-	0.94	-	-
20	-	-	1.21	1.20
24	-	2.02	1.93	2.21
48	-	4.42	5.54	5.12
72	-	6.17	7.27	8.01
96	-	7.03	9.83	9.38

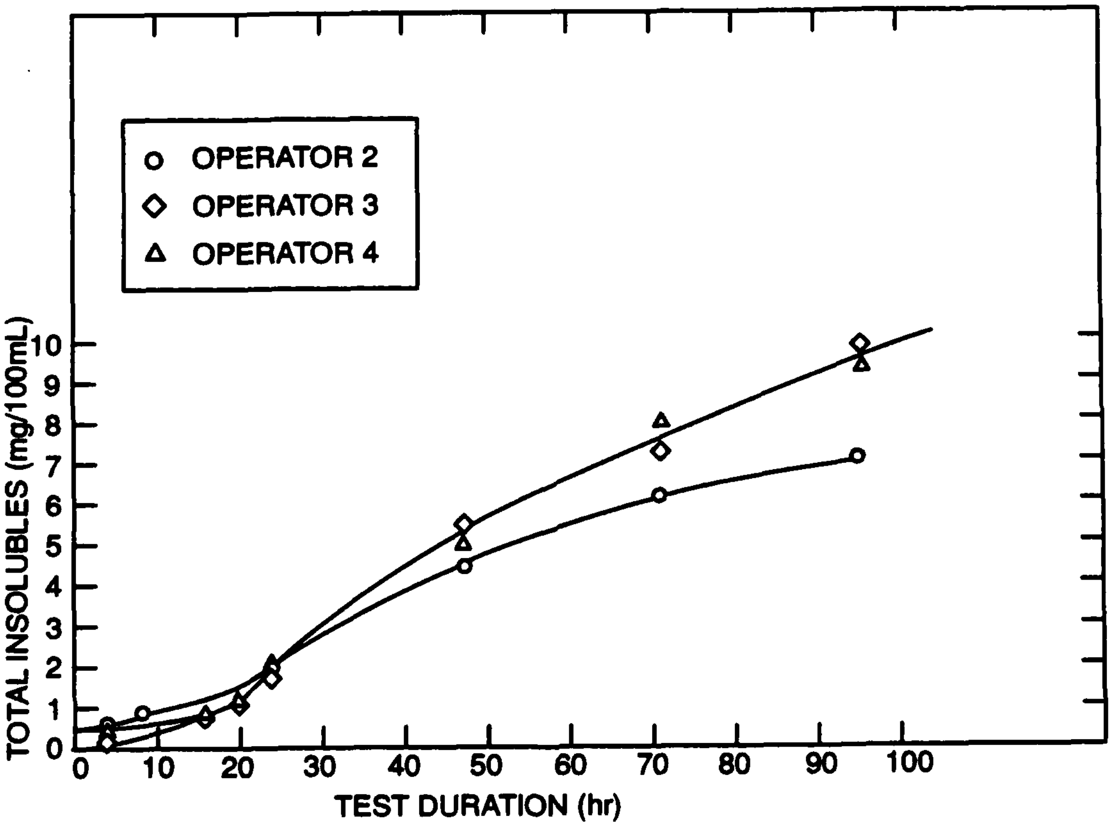

Fig. 4. Total insolubles versus D2274 test duration; initial TMP concentration of 24 mg/100 mL.

Table 6. Total insolubles versus D2274 test duration; nominal initial TMP concentration of 48 mg/100 mL (47-49 mg/100 mL).

Test Duration (hr)	Total Insolubles (mg/100 mL) Operator 1	2	3	4
4	-	0.69	0.54	0.43
5	0.10	-	-	-
8	-	0.68	-	-
20	-	-	7.69	3.84
24	6.24	9.65	11.74	3.89
48	11.88	14.70	16.93	11.16
72	13.06	17.76	21.54	13.26
96	13.98	20.64	22.25	13.92

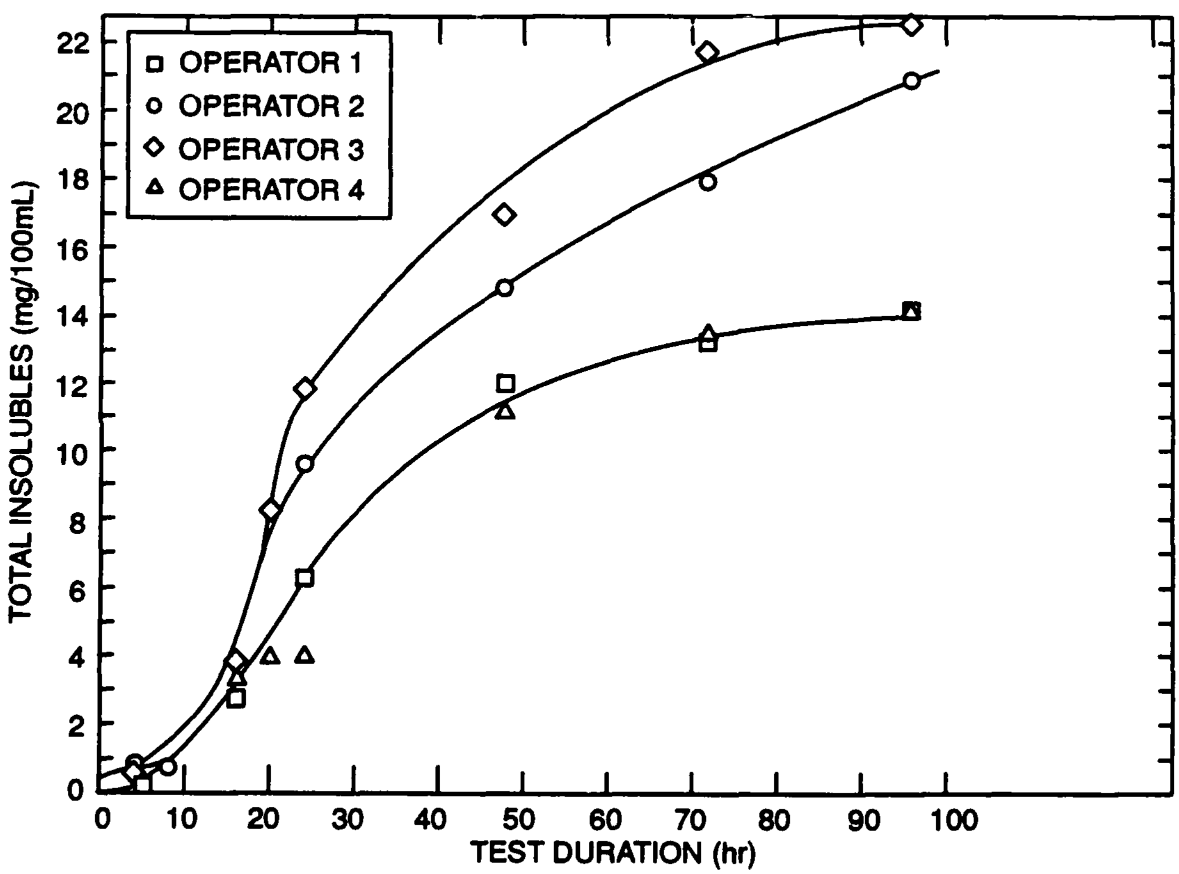

Fig. 5. Total insolubles versus D2274 test duration; nominal initial TMP concentration of 48 mg/100 mL.

Table 7. Total insolubles versus D2274 test duration; nominal initial TMP concentration of 97 mg/100 mL (96-98 mg/100 mL).

Test Duration (hr)	Total Insolubles (mg/100 mL) Operator 1	2	3	4
4	-	0.48	1.09	-
5	0.30	-	-	-
8	-	0.66	-	-
20	-	-	25.82	-
24	19.84	19.24	31.50	-
48	30.48	26.70	42.43	-
72	33.99	27.70	47.97	-
96	36.58	33.01	54.43	-

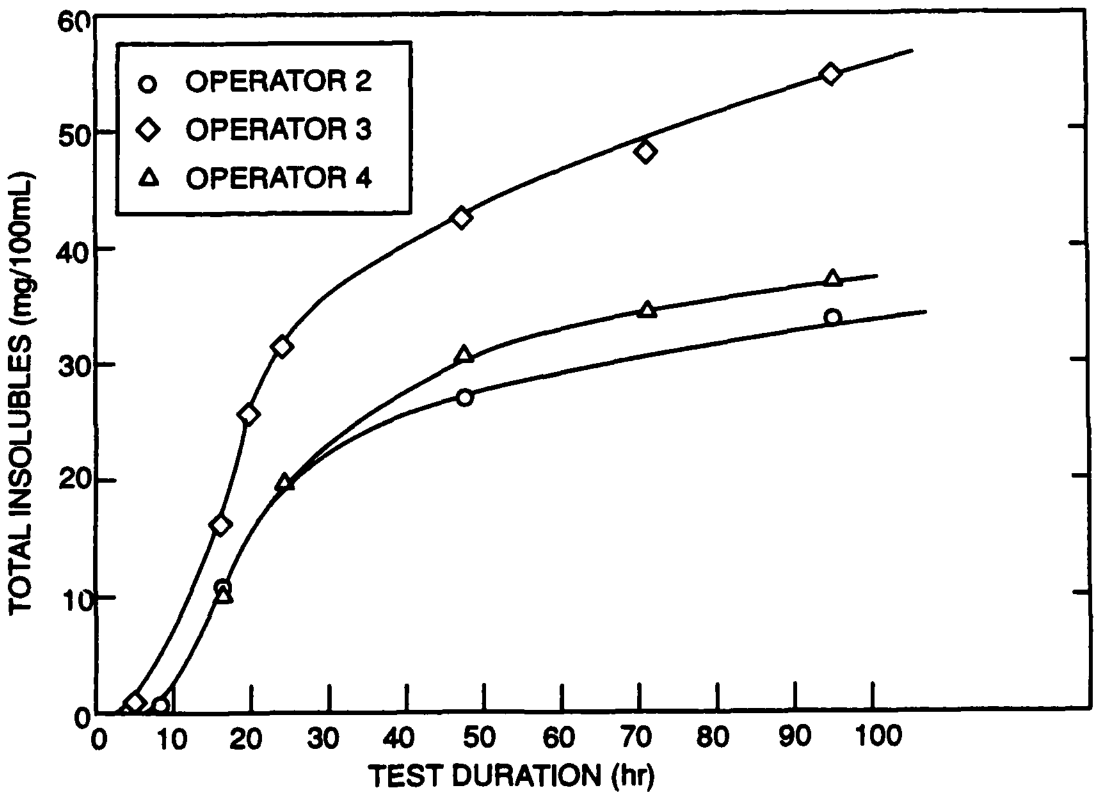

Fig. 6. Total insolubles versus D2274 test duration; nominal initial TMP concentration of 97 mg/100 mL.

Operator 4 insolubles for the 20- and 24-hr tests at TMP concentrations of 49 mg/100 mL seem low when compared with other values (see Figure 5). A sample of the fuel used in the 24-hr run was analyzed by GC and found to have only 34 mg/100 mL of TMP; this could explain the lower amount of insolubles. However, GC analysis of a sample used at the start of the 20-hr, 49 mg/100 mL run gave a much higher TMP concentration than 49 mg/100 mL; this does not explain the low insolubles obtained in that run by Operator 4.

TMP CONCENTRATION

Only samples from the runs of Operator 4 were analyzed quantitatively by gas chromatography (GC); the results appear in Table 8. Note that repeat determinations shown on the same line are analyses of fuel from replicate sample vials.

The NPD and FID calibration curves used to calculate the TMP concentrations of Table 8 were obtained using the 20, 40, and 60 mg/100 mL samples taken by Operator 4. The calculated initial TMP concentrations of several of the samples vary considerably from those reported initially. Repeat GC analysis of the same sample gave good repeatibility; therefore, the GC analysis does not appear to be the cause of the variances.

We have shown in Figure 3 that TMP freshness is an important factor in reducing the variance between operators. It appears that the accuracy with which the reference fuel concentration is prepared is another potential major source of error. An accurate standardized fuel preparation procedure must be established for any further work. Use of a gravimetric method may avoid errors in the volumetric method caused by air bubbles in the syringe or temperature variations of the TMP being measured. Freshly opened bottles of TMP and a standardized procedure to prepare the reference fuels probably would provide major improvements in reproducibility.

Figure 7 shows TMP concentration changes during an extended stress period. Concentrations were determined by GC analysis of small aliquots taken from the D2274 oxidation cells. Initial concentrations for the two curves were nominally 24 and 49 mg TMP/100 mL of n-dodecane. The concentrations of the blended fuels may not have been those intended; hence, the curves are approximations.

Table 8. Gas chromatographic analysis of ASTM D2274 samples prepared by Operator 4.

Test Duration	TMP Concentration (mg/100 mL)	
(hr)	Labeled, Initial	GC Calculated*
0	24	24.0, 23.9
0	24	17.1
0	24	24.1
0	24	25.2, 24.3
4	24	24.3, 23.4
20	24	14.2, 13.7
24	24	9.6, 9.7
48	24	1.5, 0.9, 1.4, 1.2**
72	24	0, 0
96	24	0, 0
0	49	48.3
0	49	~200***
0	49	33.7
0	49	33.4, 36.0
0	49	37.0
0	49	40.4
4	49	49.8, 46.9
20	49	19.6, 19.9
24	49	11.5, 12.0
48	49	1.1, 1.2**
72	49	0, 0
96	49	0, 0
0	20	21.0
16	20	15.3, 14.9
0	40	39.6
16	40	18.7, 20.8
0	60	60.3
16	60	23.5, 26.7
0	20 aged	~100***
16	20 aged	9.9, 8.8
0	40 aged	33.7
16	40 aged	15.1, 14.8
0	60 aged	57.6
16	60 aged	20.9

*Concentration is the average of values obtained by FID and NPD.

**These replicate concentrations were too low for FID detection.

***Exceeded upper limit of calibration range.

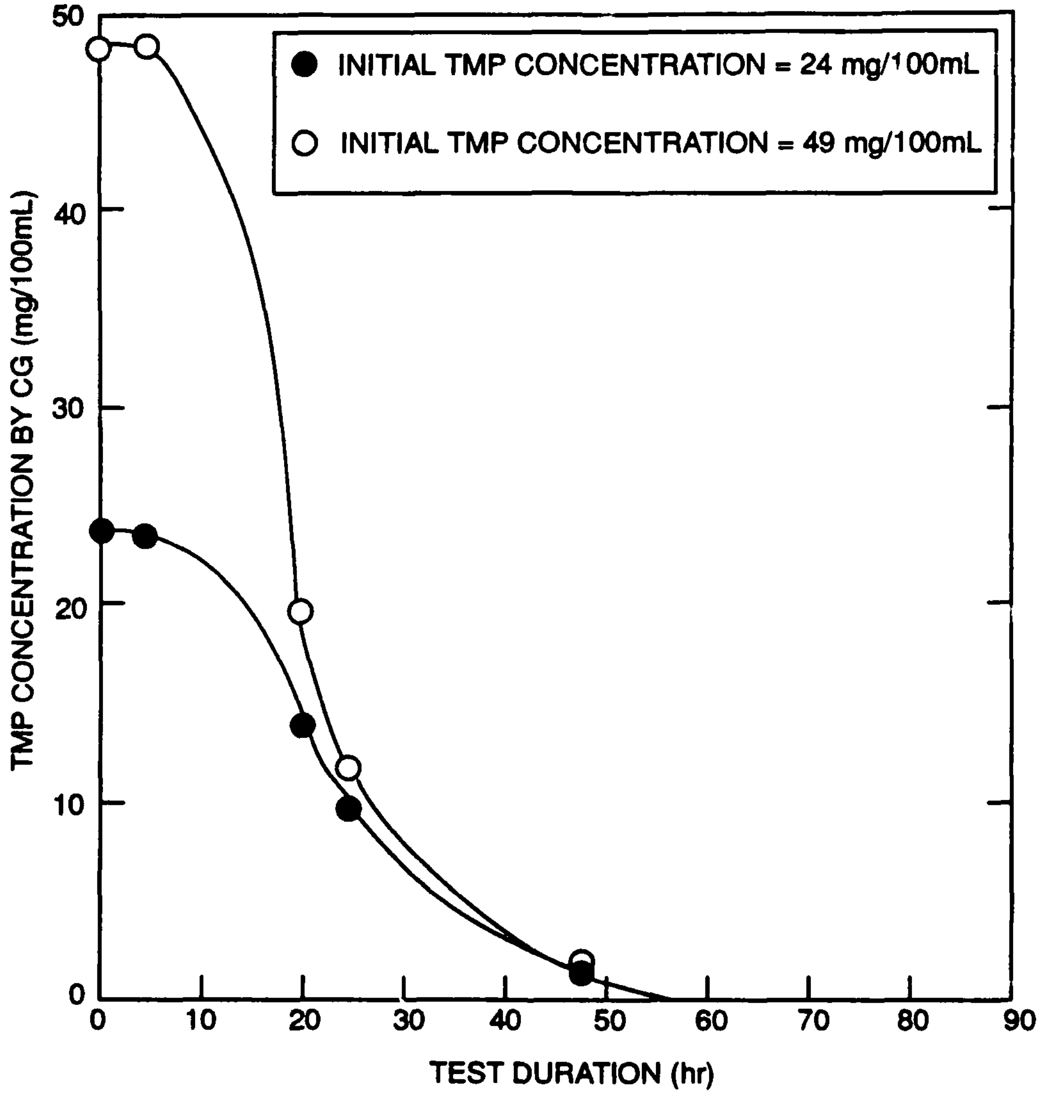

Fig. 7. TMP concentration versus D2274 test duration for two initial TMP concentrations.

CONCLUSIONS

- The reproducibility among operators was not sufficient to obtain satisfactory curves of TMP concentration versus insolubles or D2274 test duration versus insolubles.
- Reference fuels should be prepared using TMP from freshly opened bottles only; TMP starts to oxidize with exposure to air (even under refrigeration) and will yield results that are too high.

- Differences in the procedure used to prepare solutions of TMP in n-dodecane led to variations in the amounts of total insolubles formed; an accurate gravimetric (or volumetric) procedure must be established for use in further work.
- Reductions in procedural and material differences are possible and will be required to determine the level of reproducibility that can be obtained using TMP in n-dodecane as a reference fuel for D2274 tests.

RECOMMENDATIONS

- Using four operators, establish a curve for total insolubles formation from solutions of TMP in n-dodecane.
  - Use only fresh TMP.
  - Meticulously follow a prescribed gravimetric procedure to prepare the solutions.
  - Concentrate on TMP in n-dodecane concentrations below 50 mg TMP/100 mL solution.
  - Check initial TMP concentrations in the reference fuels using a GC technique.
- Develop curves of total insolubles formed in reference fuels as a function of D2274 test duration.
  - Use 12.5, 25, and 50 mg TMP/100 mL in n-dodecane.
  - Use test duration up to about 100 hr.
  - Follow the decrease in TMP concentration as a function of time using GC techniques.
- When a reliable TMP concentration versus total insolubles curve is obtained, prepare an appendix or annex for the D2274 procedure and propose its adoption to ASTM Committee D2, Section 9B on the Oxidation of Distillate Fuels.

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APPENDIX A
ASTM D2274 TEST DATA

Table A.1. Operator 1 test results.

Test Duration (hr)	TMP Concentration (mg/100 mL)	Insolubles (mg/100 mL)		
		Filterable	Adherent	Total
16	0.00	0.07	0.26	0.33
16	0.00	0.21	0.07	0.28
16	24.14	0.39	0.32	0.71
16	24.14	0.34	0.32	0.66
16	48.29	1.50	1.10	2.60
16	48.29	1.75	1.25	3.00
16	72.43	4.11	2.41	6.52
16	72.43	3.73	2.37	6.10
16	96.57	6.35	3.78	10.13
16	96.57	6.12	4.01	10.13
16	120.71	11.62	6.01	17.63
16	120.71	11.19	6.06	17.25
5	48.67	0.13	0.05	0.18
5	48.67	0.03	-0.01	0.02
24	48.67	3.47	2.64	6.11
24	48.67	3.65	2.71	6.36
48	48.67	5.43	6.40	11.83
48	48.67	5.63	6.30	11.93
72	48.67	5.68	7.24	12.92
72	48.67	5.67	7.53	13.20
96	48.67	5.15	-	-
96	48.67	5.41	8.57	13.98
5	97.34	0.12	-	-
5	97.34	0.14	0.16	0.30
24	97.34	12.17	7.55	19.72
24	97.34	12.04	7.92	19.96
48	97.34	17.00	13.33	30.33
48	97.34	17.42	13.20	30.62
72	97.34	18.33	15.44	33.77
72	97.34	18.32	15.88	34.20
96	97.34	18.79	17.78	36.57
96	97.34	19.48	17.10	36.58

Table A.2. Operator 2 test results.

Test Duration (hr)	TMP Concentration (mg/100 mL)	Insolubles (mg/100 mL)		
		Filterable	Adherent	Total
16	0.00	0.10	0.50	0.60
16	0.00	0.09	0.30	0.39
16	0.00	0.11	0.29	0.40
16	15.59	0.13	0.39	0.52
16	15.59	0.10	0.30	0.40
16	15.59	0.13	0.26	0.39
16	17.43	0.20	0.15	0.35
16	17.43	0.19	0.23	0.42
16	17.43	0.23	0.19	0.42
16	31.17	0.20	0.31	0.51
16	31.17	0.13	0.30	0.43
16	31.17	0.13	0.46	0.59
16	34.86	0.37	0.91	1.28
16	34.86	0.47	0.46	0.93
16	34.86	0.24	0.23	0.47
16	62.34	1.61	2.59	4.20
16	62.34	1.44	0.97	2.41
16	62.34	1.76	1.27	3.03
16	69.71	3.12	1.77	4.89
16	69.71	3.33	1.65	4.98
16	69.71	2.88	1.41	4.29
16	104.57	7.57	2.96	10.53
16	104.57	7.94	3.45	11.39
16	104.57	7.90	4.11	12.01
4	24.0	0.07	1.04	1.11
4	24.0	0.03	0.79	0.82
4	24.0	0.07	0.10	0.17
8	24.0	0.07	1.57	1.64
8	24.0	0.06	0.80	0.86
8	24.0	0.03	0.29	0.32
24	24.0	0.57	0.89	1.46
24	24.0	0.71	1.24	1.95

Table A.2. (Continued)

Test Duration (hr)	TMP Concentration (mg/100 mL)	Insolubles (mg/100 mL)		
		Filterable	Adherent	Total
24	24.0	0.77	1.89	2.66
48	24.0	1.86	2.56	4.42
48	24.0	1.60	2.57	4.17
48	24.0	2.11	2.56	4.67
72	24.0	2.99	3.53	6.52
72	24.0	3.17	4.06	7.23
72	24.0	2.73	2.04	4.77
96	24.0	3.24	3.76	7.00
96	24.0	3.29	4.40	7.69
96	24.0	3.39	3.00	6.39
4	47.0	0.07	0.43	0.50
4	47.0	0.13	0.60	0.73
4	47.0	0.17	0.68	0.85
8	47.0	0.07	0.17	0.24
8	47.0	0.57	0.90	1.47
8	47.0	0.09	0.23	0.32
8	47.0	0.07	0.63	0.70
8	47.0	0.10	0.59	0.69
24	47.0	6.07	3.74	9.81
24	47.0	6.06	3.97	10.03
24	47.0	5.09	4.01	9.10
48	47.0	5.19	8.30	13.49
48	47.0	6.83	9.30	16.13
48	47.0	5.37	9.11	14.48
72	47.0	6.99	11.40	18.39
72	47.0	2.73	10.00	12.73
72	47.0	6.43	15.72	22.15
96	47.0	12.11	12.64	24.75
96	47.0	8.46	7.57	16.03
96	47.0	8.97	13.64	22.61
96	47.0	12.13	10.40	22.53
96	47.0	9.60	7.69	17.29

Table A.2. (Continued)

Test Duration (hr)	TMP Concentration (mg/100 mL)	Insolubles (mg/100 mL)		
		Filterable	Adherent	Total
4	96.0	0.07	0.37	0.44
4	96.0	0.04	0.37	0.41
4	96.0	0.17	0.41	0.58
8	96.0	0.40	0.39	0.79
8	96.0	0.29	0.14	0.43
8	96.0	0.44	0.31	0.75
24	96.0	11.74	6.64	18.38
24	96.0	9.74	7.63	17.37
24	96.0	14.49	7.47	21.96
48	96.0	12.89	12.64	25.53
48	96.0	16.09	9.74	26.06
48	96.0	14.13	14.37	28.50
72	96.0	9.51	9.50	19.01
72	96.0	16.54	13.61	30.15
72	96.0	19.76	14.17	33.93
96	96.0	12.09	14.13	26.33
96	96.0	18.96	14.77	33.73
96	96.0	21.67	17.29	38.96

Table A.3. Operator 3 test results.

Test Duration (hr)	TMP Concentration (mg/100 mL)	Insolubles (mg/100 mL)		
		Filterable	Adherent	Total
16	0.0	0.01	0.04	0.05
16	0.0	0.06	-0.03	0.03
16	24.0	0.40	0.50	0.90
16	24.0	0.35	0.40	0.75
16	49.0	1.76	1.90	3.66
16	49.0	1.58	2.30	3.88
16	75.0	6.37	3.70	10.07
16	75.0	1.68	7.30	8.98
16	98.0	11.58	4.90	16.48
16	98.0	4.58	11.60	16.18
16	150.0	22.00	9.90	31.90
16	150.0	21.03	11.00	32.03
4	24.0	0.03	0.10	0.13
4	24.0	0.00	0.10	0.10
20	24.0	0.66	0.60	1.26
20	24.0	0.75	0.40	1.15
24	24.0	0.29	1.50	1.79
24	24.0	0.76	1.30	2.06
48	24.0	1.80	4.20	6.00
48	24.0	1.27	3.80	5.07
72	24.0	2.68	4.50	7.18
72	24.0	2.95	4.40	7.35
96	24.0	3.39	6.30	9.69
96	24.0	3.77	6.20	9.97

Table A.3. (Continued)

Test Duration (hr)	TMP Concentration (mg/100 mL)	Insolubles (mg/100 mL)		
		Filterable	Adherent	Total
4	49.0	0.11	0.40	0.51
4	49.0	0.07	0.50	0.57
20	49.0	3.51	4.20	7.71
20	49.0	1.17	6.50	7.67
24	49.0	6.30	7.30	13.60
24	49.0	1.87	8.00	9.87
48	49.0	5.66	10.90	16.56
48	49.0	6.39	10.90	17.29
72	49.0	7.71	13.50	21.21
72	49.0	7.07	14.80	21.87
96	49.0	9.11	13.20	22.31
96	49.0	7.88	14.30	22.18
4	98.0	0.41	0.70	1.11
4	98.0	0.57	0.50	1.07
20	98.0	9.23	16.30	25.53
20	98.0	8.80	17.30	26.10
24	98.0	17.35	13.20	30.55
24	98.0	16.55	15.90	32.45
48	98.0	17.01	25.50	42.51
48	98.0	18.84	23.50	42.34
72	98.0	19.30	27.80	47.10
72	98.0	21.74	27.10	48.84
96	98.0	24.09	30.40	54.49
96	98.0	25.27	29.10	54.37

Table A.4. Operator 4 test results.

Test Duration (hr)	TMP Concentration (mg/100 mL)	Insolubles (mg/100 mL)		
		Filterable	Adherent	Total
16	0.0	-0.25	0.50	0.25
16	0.0	-0.02	0.00	-0.02
16	20.0	0.11	0.70	0.81
16	20.0	0.18	0.50	0.68
16	20.0 (aged)	0.87	0.90	1.77
16	20.0 (aged)	0.83	1.10	1.93
16	24.0	0.41	0.60	1.01
16	24.0	0.53	0.20	0.73
16	40.0	0.56	1.70	2.26
16	40.0	1.23	1.10	2.33
16	40.0 (aged)	3.57	2.50	6.07
16	40.0 (aged)	3.81	2.70	6.51
16	49.0	2.11	1.00	3.11
16	49.0	1.79	1.70	3.49
16	60.0	2.73	2.40	5.13
16	60.0	3.21	2.30	5.51
16	60.0	2.04	4.30	6.34
16	60.0	3.92	2.80	6.72
16	60.0 (aged)	7.97	4.40	12.37
16	60.0 (aged)	7.76	2.90	10.66
16	75.0	5.61	2.60	8.21
16	75.0	5.29	3.30	8.59
16	98.0	7.96	5.60	13.56
16	98.0	8.80	4.00	12.80

Table A.4. (Continued)

Test Duration (hr)	TMP Concentration (mg/100 mL)	Insolubles (mg/100 mL)		
		Filterable	Adherent	Total
4	24.0	0.04	0.20	0.24
4	24.0	0.04	0.90	0.94
20	24.0	0.33	0.90	1.23
20	24.0	0.36	0.80	1.16
24	24.0	0.72	1.60	2.32
24	24.0	0.79	1.30	2.09
48	24.0	1.89	3.30	5.19
48	24.0	2.15	2.90	5.05
72	24.0	2.65	5.60	8.25
72	24.0	2.97	4.80	7.77
96	24.0	3.69	5.70	9.39
96	24.0	3.87	5.50	9.37
4	49.0	0.06	0.40	0.46
4	49.0	0.09	0.30	0.39
20	49.0	1.71	1.90	3.61
20	49.0	2.06	2.00	4.06
24	49.0	1.53	2.20	3.73
24	49.0	1.75	2.30	4.05
48	49.0	4.68	7.00	11.68
48	49.0	5.13	5.50	10.63
72	49.0	5.14	7.50	12.64
72	49.0	4.08	9.80	13.88
96	49.0	5.66	8.60	14.46
96	49.0	4.58	8.80	13.38

REFERENCES

1. White, E.W., M.D. Klinkhammer, and K.W. Flohr, "The Development of Reference Fuels for Use with the ASTM D2274 Test for Fuel Storage Stability," Conference Proceedings of the Third International Conference on Stability and Handling of Liquid Fuels, London, UK, p. 554-565, (13-16 Sep 1988).

2. Bowen, R.J., and E.W. White, "Testing and Qualification of a Twelve-Cell Oxidation Apparatus for Conducting ASTM D2274 Stability Tests," DTRC Report SME-86/01, ABCA/3/US/F-2/86 (Mar 1986).

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